

BIODIESEL PRODUCTION FROM JATROPHA CURCAS VIA TWO- STEPS CATALYZED PROCESS

GUGANESWARAN A/L SINNATHAMBY

**A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering**

Faculty of Chemical & Natural Resources Engineering

University Malaysia Pahang

NOVEMBER 2010

ABSTRACT

Biodiesel, an alternative renewable fuel made from transesterification of vegetable oil with alcohol, is becoming more readily available for use in blends with conventional diesel fuel for transportation applications. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids such as inedible oils, animal fats, waste food oil and by products of the refining vegetables oils. The fact that *Jatropha* oil cannot be used for nutritional purposes without detoxification makes its use as energy or fuel source very attractive. The effect of main factor which are, temperature, particle size of the meal and reaction time were investigated to optimize the extraction operating conditions for achieving maximum oil yield. The lipid fraction of *Jatropha curcas* oil seed were extracted and to study the analyzed for their chemical and physical properties such as acid value, percentage free fatty acids (% FFA), iodine value, peroxide value and saponification value as well as viscosity, and density. The fatty acid composition of the extracted lipid was revealed using the (GCMS) method. Biodiesel production process is the transesterification of the used two-steps catalyzed process with *jatropha* oil and methanol, in the presence of alkali catalyst, to yield the ethyl ester as a product and glycerine as a by-product. In the acid treatment or the acidcatalyzed esterification, the temperature is set at 40°C, acid catalyst of 2%w/wH₂SO₄. These studies have been performed based on 3 effect, temperature, catalyst concentration and time. As a result, the best condition that has been determined for maximum biodiesel production were 1.5% catalyst concentration of potassium hydroxides based on weight of *jatropha curcas* oil that were used methanol to *jatropha curcas* oil of 6:1 and, process were done at temperature 60°C and the time is about 60 minutes. Biodiesel yield and moisture content in biodiesel production from *jatropha curcas* oil were measured. Oil yield content of *jatropha* kernel was found about 50–60% for different extraction time. Both oleic acid (45.24%) and linoleic acid (31.58%) were detected as the dominant fatty acids while palmitic acid and stearic acid were the saturated fatty acids found in the *Jatropha curcas* oil. These processes which using ultrasonic reactor is easy and faster than other biodiesel production process because cavities caused by the ultrasound at the catalyst surface increase the catalyst activity and reduce the activation over potential loss.

ABSTRAK

Biodiesel, bahan bakar alternatif boleh diperbaharui yang terbuat dari pengtransesteran minyak sayuran dengan alkohol, menjadi lebih mudah sedia untuk digunakan dalam campuran dengan bahan bakar solar konvensional untuk aplikasi pengangkutan. Salah satu cara untuk mengurangkan kos pengeluaran biodiesel adalah menggunakan bahan baku lebih murah yang mengandungi asid lemak seperti minyak dimakan, lemak haiwan, minyak sisa makanan dan oleh produk-produk dari pemurnian minyak sayuran. Pengaruh faktor utama iaitu, suhu, saiz zarah dari masa makan dan reaksi yang diselidiki untuk mengoptimumkan ekstraksi keadaan operasi untuk mencapai hasil minyak maksimum. Pecahan lemak minyak biji jatropha di ambil dan untuk mempelajari dianalisa kimia dan sifat fizikal seperti bilangan asid, asid peratusan lemak bebas (% FFA), nilai iodin, nilai peroksida dan nilai penyabunan serta viskositi, dan kerapatan . Komposisi asid lemak dari lipid diekstrak diturunkan dengan menggunakan kaedah (GCMS). proses pengeluaran Biodiesel adalah pengtransesteran dari dua digunakan-langkah proses mangkin dengan minyak jatropha dan metanol, dengan adanya mangkin alkali, untuk menghasilkan ester etil sebagai produk dan gliserin sebagai produk-oleh. Pada perlakuan acid atau pengesteran acidcatalyzed, suhu ditetapkan pada 40°C , asid mangkin 2% w/wH₂SO₄. Pengajian-kajian ini telah dilakukan berdasarkan 3 kesan, suhu, konsentrasi mangkin dan masa. Akibatnya, keadaan terbaik yang telah ditetapkan untuk pengeluaran biodiesel maksimum adalah 1.5% mangkin konsentrasi kalium hidroksida berdasarkan berat minyak jatropha yang digunakan metanol untuk minyak jatropha dari 6:1 dan, proses dilakukan pada suhu 60°C dan masa sekitar 60 minit. Biodiesel hasil dan kadar air dalam pengeluaran biodiesel dari minyak jatropha diukur. Menghasilkan kandungan minyak jatropha kernel dijumpai sekitar 50-60% untuk masa ekstraksi yang berbeza. Kedua-dua asid oleik (45,24%) dan asid linoleat (31,58%) yang dikesan sebagai asid lemak yang dominan, manakala asid palmitat dan asid stearat adalah asid lemak tepu ditemui di minyak jatropha.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	
	DEDICATION	
	ACKNOWLEDGEMENT	i
	ABSTRACT	ii
	ABSTRAK	iii
	TABLE OF CONTENTS	iv
	LIST OF TABLES	viii
	LIST OF FIGURES	ix
	LIST OF SYMBOLS	xi
1.0	INTRODUCTION	1
	1.1 Background of the study	1
	1.2 Problem statement	4
	1.3 Objective	5
	1.4 Scope of research	5
2.0	LITERATURE REVIEW	6
	2.1 Introduction	6
	2.2 Biodiesel	8
	2.2.1 Characteristic of biodiesel	9
	2.3 Transesterification	10
	2.4 Glycerine washing and methanol recovery	11
	Process	
	2.5 Glycerine	11
	2.6 Alkali catalyst	12
	2.7 Acid catalyst	12
	2.8 Amount of Catalyst	13

2.9 Ultrasonic Transesterification	14
2.10 Ultrasound	16
2.11 Acid-Catalyzed Pre-Treatment	17
2.12 Gas Chromatography	19
3.0 METHODOLOGY	20
3.1 Materials	20
3.2 Raw material preparation	20
3.3 Optimization of oil extraction	20
3.4 Chemical and Physical analysis of seed oil	21
3.4.1 Acid value, % FFA.	21
3.4.2 Iodine value	21
3.4.3 Saponification value	21
3.4.4 Peroxide value	22
3.4.5 Kinematics Viscosity	22
3.4.6 Density	22
3.4.7 Analysis of Fatty Acid Compositions	22
3.5 Catalyst Preparation	23
3.6 Acid-Catalyzed Esterification	23
3.7 Alkali Catalyzed Transesterification	24
3.8 Draining of Glycerol	27
3.9 Methanol Recovery	28
3.10 Washing	29
3.11 Biodiesel Yield	29
3.12 Moisture content	30
3.13 flow chart	31

4.0	RESULTS AND DISCUSSION	32
4.1	Introduction	32
4.2	Effect of reaction time on oil extraction	32
4.3	Effect of particle size on oil extraction	35
4.4	Chemical and physical properties of extracted oil	36
4.5	Effects of catalyst concentration	38
4.6	Effects of temperature	41
4.7	Effects of time	43
5.0	CONCLUSION AND RECOMMENDATION	46
	REFERENCE	48
	APPENDIX	51

LIST OF TABLES

TABLE NO	TITLE	PAGE
2.1	Comparison of different types of catalyst	19
3.1	Weight of Substances needed during the acid catalyzed	30
3.2	Fixed and manipulated parameter for alkali catalyzed	31
3.3	Fixed and manipulated parameter for alkali catalyzed transesterification phase II	32
3.4	Weight of alkali Catalyst	33
4.1	Particle size 10 μ m	38
4.2	Particle size 1mm	39
4.3	Fatty acid composition & Chemical and physical properties of Jatropha Curcas oil.	42
4.4	Analysis data on biodiesel samples based on different catalyst concentration	44
4.5	Analysis data on biodiesel samples based on different Temperature	47
4.6	Analysis data on biodiesel samples based on different time	49

LIST OF FIGURES

FIGURE NO	TITLE	PAGE
2.1	Example of biodiesel	15
2.2	Consecutive steps of transesterification	16
2.3	Result of rapeseed oil transesterification with potassium hydroxide using conventional agitation and ultrasonication	21
2.4	Esterification of FFAs to ester using methanol & acid catalyst	24
3.5	Methanol recovery	34
3.6	Biodiesel after 1 hour washed with hot water	35
4.1	Graph percentage of extracted oil vs time for particle size 10 μ m	39
4.2	Graph percentage of extracted oil vs time for particle size 1mm	40
4.3	graph show comparison on extracted oil yield vs time for different particle size	41
4.4	Percentage of biodiesel yield vs. catalyst concentration	45
4.5	Percentage of moisture content vs. catalyst concentration	45
4.6	Graph bodiesel yield vs temperature	47
4.7	Graph percentage of moisture content vs. temperature	48
4.8	Graph percentage of biodiesel yield vs. time	50
4.9	Graph percentage of moisture content vs. time	50

LIST OF SYMBOLS

$^{\circ}\text{C}$ - Temperature

l - Length

ρ - Density

s - Time (second)

M - Mega

Hz - Hertz

ml - Milimeter

G - Gram

Wt - Weight Percent

CHAPTER I

INTRODUCTION

1.1 Background

Alternative fuels for diesel engines are becoming increasingly important due to diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum-fuelled engines. The energy source, fossil fuel, upon which we have come to rely on so deeply is in higher demand than ever before, that more energy is needed all around to fulfill this demand. (Pramanik , 2003). Fossil fuel alone seems to be insufficient to cater to the needs of the global community. In light of this, it is in the world's best interest to devote a substantial amount of resources towards alternative forms of energy. Biofuel , as biodiesel in this context, is at the forefront of these alternatives due to its ability to fuel conventional diesel engines with minimum or no modifications, as well as form blends with fossil diesel.

Biodiesel is defined as fatty acid methyl esters prepared from any kind of feedstock including vegetable oils, animal fats, single cell oils, and waste material. Fatty acid ethyl esters can also be defined as and used to produce biodiesel. (Knothe et al., 2002). However, due to the relatively high price of ethanol compared to methanol, the use of ethyl esters has not so far been established. The preparation of fatty acid methyl esters can be achieved by a process called transesterification, which is the exchange of alcohol or acid moiety of an ester.

Alcoholysis is the transesterification of an ester with an alcohol, in which methanolysis is the term used in the case of methanol. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide, and produces new chemical compounds called methyl esters. It is these esters that have come to be known as biodiesel. Because its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. (Veljkovic' et al., 2006). Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels. (Openshaw et al, 2000). Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxics than when operated on petroleum-based diesel fuel.

All feedstocks that contain fatty acids or glycerol can be used for biodiesel production including *jatropha curcas* oil. In European countries, rapeseed oil is used due to its widespread availability. Soybean oil is used in the Unites States of America, while palm oil is used widely in tropical regions such as Malaysia. The use of methyl esters as fuel requires a low proportion of saturated fatty acids in order to make the fuel function at low temperatures. In colder climates, rapeseed oil and olive oil have proven to be one of the best options. The usage of palm oil is ideal in Malaysia due its abundant availability as well as its suitability in warm climates. Palm oil can also be used as blends with other types of oil. Feedstock chosen is also influenced by national and international specifications of biodiesel that need to be fulfilled.

1.2 Problem Statement

The current energy crisis has beckoned upon us to look towards an energy alternative that is feasible and sustainable in the long run. Being a direct solution to the current shortage of liquid fuel, biodiesel is one of the most popular alternatives of all time. This research seeks to solve this uncertainty in feedstock sustainable selection, of the researched types of biodiesel feedstock, namely *Jatropha curcas* oil. *Jatropha curcas* is a wonder plant with a variety of applications and enormous economic potentials. Oil from the seeds can be used as alternative fuel and for making biodiesel which aims to overcome energy crisis problems. In this study, extraction of *Jatropha curcas* oil from seeds was optimized using organic solvent based on the amount of the extracted oil. Using the virgin oil as a feedstock we would not require additional steps in biodiesel production, such as prefiltration and preheating as well as a relatively high catalyst concentration, that may incur additional costs of processing.

Ultrasonic transesterification in biodiesel production can reduce processing time to 25% of the time needed otherwise. Industrially, along with producing 99% yield, it is highly more efficient than conventional agitation that can take up to 12 hours, reducing this time frame to less than 60 minutes. The amount of catalyst required can also be reduced by up to 50% due to the increased chemical activity in the cavitations formed due to ultrasonication. In addition to this, it also extensively reduces the amount of excess alcohol required for processing while increasing the purity of the glycerin formed. This type of processing, coupled with a comparative research of the two said feedstock, would provide a feasible, sustainable, and efficient choice of feedstock for biodiesel production.

1.3 Objectives

The main objective of the present work was to study on the effect of two step catalyst reaction in producing biodiesel from *jatropha curcas* oil using ultrasonic transesterification, with alkali catalyst potassium hydroxide and , acid catalyst of 2%w/wH₂SO₄ as the catalyst. A second objective was to Optimized of oil extraction from *jatropha curcas* seeds.

1.4 Scope of Research

1.4.1 To comparatively study the effect of catalyst concentration and reaction time on the yield and purity of biodiesel produced from *jatropha curcas* oil using ultrasonic transesterification.

1.4.2 The effect main factor which are temperature, particle size of the meal and reaction time were investigated to optimize the extraction operating conditions for achieving maximum oil yield.

1.4.3 To comparatively study the combustion characteristics of biodiesel produced from *jatropha curcas* oil and analyze the products using Gas Chromatography.

1.5 Rationale and Significance

The rationale of this proposed research project is to provide empirical evidence to compare the purity and yield between biodiesel production from *Jatropha curcas*. The results of this research would signify the identification of a feedstock for biodiesel production that is feasible, sustainable and efficient for Malaysia. The identification of this feedstock will be a basis for the production of biodiesel on an industrial scale to counter the current global shortage of fuel.

The numerous advantages of using Ultrasonic transesterification would bring about volumes of significance in the biodiesel production industry. This is due to the fact that aside from giving relatively high yield, it would monumentally reduce the length of processing time needed for production, and this would go well to supply the ever increasing rate of demand for alternative liquid fuel. With Ultrasonic transesterification, the biodiesel production industry in Malaysia would be able to cater to the needs of Malaysians at a faster rate, thereby eliminating the need for any dependence on foreign alternative fuel that may arise in the future. Malaysia would be able to deal with its own fuel crisis, at an optimal rate using its abundant feedstock resources and ultrasonic transesterification.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Diesel-petroleum based has released problems such as toxicity, water, land and air pollution, fire risk, non-biodegradability and limited resources had opened a unique opportunity to produced new environmental acceptable fuel and lubricants derived from natural ester like vegetable oil. Reported that, the world production of 17 major oils and fats are over 100 billion tones and out this 79% are from vegetable oil (Hamm and Hamilton, 2002).

Research, development and application of vegetable based oil in industrial and automotive sectors are rapidly increasing. The attractive part of vegetable oil is they are neutral, non-toxic, biodegradable, and relatively non-polluting and derived from renewable raw material. During the last decade, due to strict government and environment regulation almost of all country in the world, there has been constant demand for environmentally friendly fuel (Reijnders , 2006). Most of fuel originates from petroleum stock which is toxic to environment and difficult to dispose. Vegetable oils with high oleic acid content are considered to be potential candidates to substitute conventional mineral oil base fuel oils and synthetic esters.

Although biodiesel cannot entirely replace petroleum-based diesel fuel, there are at least five reasons that justify its development (Gerpen, 2005):

- 1) It provides a sufficient market for excess production of vegetable oils and fats.
- 2) It decreased, although will not eliminate, most country's dependencies on imported petroleum.
- 3) Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle. A life cycle analysis of biodiesel showed that generally CO₂ emissions were reduced by 78% compared with petroleum-based diesel fuel (Sheehan *et al*, 1998).
- 4) The exhausts emissions of carbon monoxide, unburned hydrocarbons, and particulate emissions from biodiesel are lower than with regular diesel fuel. Unfortunately, most emissions test has shown a slight increase of nitrogen oxides (NO_x).
- 5) When added to regular diesel fuel in an amount equal to 1-2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel.

In 1997, the production of biodiesel fuel was 550,000 tons in Europe, 10,000 tons in Malaysia and 9000 tons in North America. In 2000, the annual production of biodiesel in Europe was 1,210,000 tons. The production increased 2.2 times in three years (Kann *et al*, 2002).

2.2 Biodiesel

At the forefront of the array of alternative energy sources that are being researched and developed today, is biofuel. Having physical and chemical properties that are compatible with its fossil counterpart has placed biodiesel as one of the most suitable alternatives to complement today, and perhaps even replace fossil diesel tomorrow. Its ability to fuel conventional diesel engines with minimum or no modifications, and to form blends with fossil diesel make it the most practical, and feasible alternative energy source to invest in.

There are many ways how biodiesel serves to benefit the environment more than fossil diesel. One major aspect of life cycle assessments is the potential of global warming, expressed as carbon dioxide, CO₂ equivalents. CO₂ is produced during the whole production process of fuels, biological based and fossil based alike. Due to the positive energy balance of biodiesel and the fact that biodiesel mainly consists of renewable material one could expect a large saving of greenhouse gases compared to fossil fuel. Now, while this remains true in the case of CO₂, certain parties argue that if other greenhouse gases like N₂O and CH₄ are considered, which have higher global warming potential, the advantages of biodiesel are slightly diminished. Even so, the relative savings of greenhouse gases for the use of biodiesel over fossil diesel is 2.7kg of saved CO₂ equivalents for every kg of substituted fossil diesel fuel. Pure biodiesel is also completely free of sulfur and, this inadvertently reduces sulfur dioxide exhaust from diesel engines to virtually zero.

2.2.1 Characteristic of Biodiesel

Biodiesel is well known as an alternative fuel for diesel engines that is chemically produced by reacting the virgin or used vegetable oil or animal fats with an alcohol such as methanol in order to accelerate the reaction (Leung *et al*, 2006).

Figure 2.1 shows an example of biodiesel. However, its colors can be varied between golden and dark brown because it depends on the production feedstock. It is practically immiscible with water, has high boiling point and low vapor pressure. Typical methyl ester biodiesel has a flash point of $\sim 150^{\circ}\text{C}$ (300°F), making it rather non-flammable. Biodiesel has density of $\sim 0.88\text{g/cm}^3$, less than water. Biodiesel that is unpolluted with starting material can be regarded as non-toxic. It also has similar viscosity with petrodiesel that produces from petroleum.



Figure 2.1: Example of biodiesel

Moreover, biodiesel is also a clean burning diesel fuel replacement made from natural, renewable sources, such as new and used vegetable oils or animal fats. It will run in any diesel engine with a little or no modification and can be mixed with regular diesel fuel in any ratio. Biodiesel is non-toxic and biodegradable.

2.3 Transesterification

Transesterification, is also known as Alcoholysis. It is the displacement of alcohol from an ester by another alcohol in a similar manner in that of hydrolysis, except than alcohol is used instead of water. Each reaction step is reversible. This process is used widely in reducing the viscosity of vegetable oils. Methanol and ethanol are most frequently used, especially methanol because of its low cost and its physical and chemical advantages. If methanol is used in this process it is called methanolysis. Thus, fatty acid methyl esters or FAMES, known as biodiesel fuel are formed. The FAME's obtained by transesterification are similar to conventional diesel fuel in its main characteristics and can be used as an alternative fuel or used in blends with fossil diesel for diesel engines. (Song *et al.*, 2007)

Figure 2.2 shows the overall process of transesterification which is normally series of three consecutive steps which are reversible reactions. In the first steps diglycerides, are obtained from triglycerides. From diglycerides, monoglycerides are then produced. In the last step, from monoglycerides, glycerol is formed. In all these reactions, esters are produced. The excess of alcohol is usually more appropriate to improve the reaction towards the desired final product (Marchetti *et al.*, 2007).

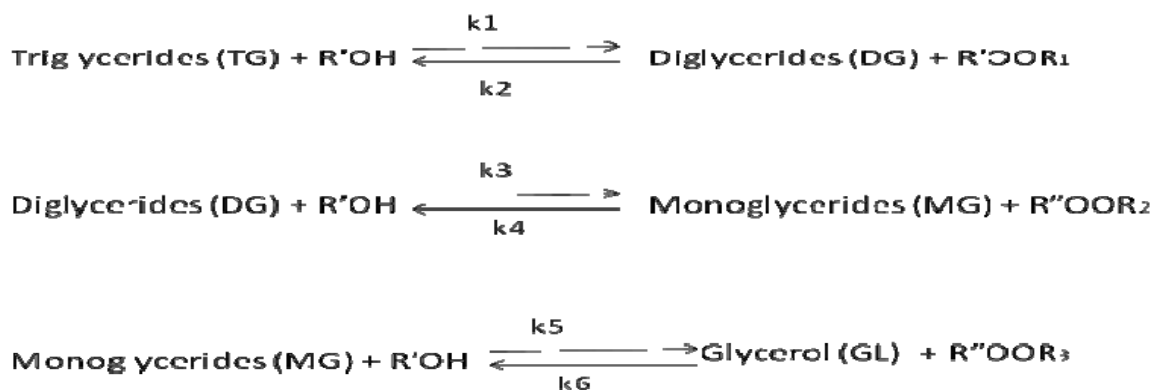


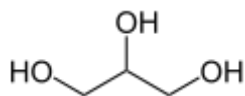
Figure 2.2: Consecutive steps of transesterification

2.4 Glycerine washing and methanol recovery process

The transesterification reaction between oil and an alcohol such as methanol to produce biodiesel yields glycerine as a byproduct. This glycerine needs to be separated out of the product and the methanol recovered. Since the methanol used in the reaction is in excess to allow for sufficient reaction, a considerable amount of methanol can be recovered for reuse. Among the methods available for the removal of methanol are vacuum evaporation, distillation, and water washing. An economical method of methanol removal would be the water washing method since it acquires a relatively low cost. The glycerine can be removed from the product by decantation.

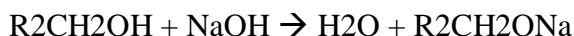
2.5 Glycerine

Glycerine, a byproduct from the transesterification reaction to produce biodiesel, is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. It also goes by the names, glycerol and glycerin. Glycerine is a sugar alcohol of sweet-taste and low toxicity. It has three hydrophilic alcoholic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. Its substructure is a central component of many lipids. (Subramanian *et al.*, 2000)



2.6 Alkali catalyst

Either sodium hydroxide (NaOH) or potassium hydroxide (KOH) can be used with methanol or ethanol and the chosen oil. It is best to produce the alcoxy before the reaction to obtain a better global efficiency. The alcoxy reaction is



The alcohol–oil molar ratio that should be used varies from a ratio of 1:1–6:1. However, 6:1 is the most used ratio, leading to an important conversion for the alkali catalyst without using an immense amount of alcohol. The types of alcohol considered are usually methanol and ethanol. Methanol has fewer safety problems because it is less toxic compared to ethanol, thus its usage would have significantly smaller safety issues. The amount of catalyst that should be added to the reactor varies from 0.5% to 1% w/w. The alkali process is more efficient and less corrosive than the acid process. (J.M. Marchetti *et al.*, 2003).

2.7 Acid catalyst

In this process, the triglycerides are used with the alcohol. In this case, instead of a base an acid is used. The most common acid used is sulfuric acid sometimes sulfonic acid. This catalyst gives a very high yield in esters but the reaction occurs very slowly. It normally takes more than a day to finish. If an excess of alcohol is used in the experiment, a better conversion of triglycerides is obtained. However, recovering glycerol becomes more difficult, which is why an optimal relationship between the alcohol and raw material should be determined experimentally considering each process as a new problem. The operation condition is usually in the form of a molar ratio of 30:1. The amount of catalyst that should be added to the reactor varies from 0.5 to 1 mol% (Song *et al.*, 2007).

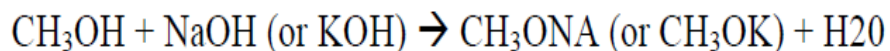
2.8 Amount of Catalyst

The three catalyst (KOH, NaOH, and CH₃ONa) exhibit the same trend on the conversion of the TG to esters but different amount of catalyst will be required to achieve the same conversion (Leung *et al*, 2006). Table 2.1 shows the maximum ester content of the biodiesel product was reached at 1.1, 1.3, and 1.5wt% of the catalyst concentration for NaOH, CH₃ONa, and KOH respectively. The amount of NaOH used was smaller than those of KOH and CH₃ONa for the same mass feedstock oil, since NaOH has the smallest molar mass (40 g/mol), followed by CH₃ONa (54 g/mol), and KOH (56 g/mol). However, in term of concentration, CH₃ONa was about 10% lesser than NaOH and KOH.

Table 2.1: Comparison of different types of catalyst in the transesterification of JCO (temperature of 70°C, reaction time of 30 minutes, methanol/oil ratio of 7.5:1)

	Concentration of the catalyst (wt%, by weight of crude oil)	Ester content (wt%)	Product yield (wt%)
NaOH	1.1	94	85.3
KOH	1.5	92.5	86
CH ₃ ONa	1.3	92.8	89

As shown in Table 2.2, the biodiesel yield with NaOH and KOH as catalyst were lower than CH₃ONa. This happen during the preparation of the catalyst NaOH or KOH is added and dissolved in the anhydrous methanol forming sodium or potassium methoxide together with small amount of water according to the following equilibrium equation.



The water in the reaction system predominantly reacts with oils (TG) and the Na^+ (or K^+) to form sodium (or potassium) soaps. This is the saponification reaction of TGs leading to the loss of TGs and hence reduction in final product yields. On the other hand, the pure CH_3ONa catalyst only dissociates into CH_3O^- and Na^+ without forming any water as side product in the reaction that will cause a drop in product yield.

2.9 Ultrasonic Transesterification

Ultrasonication increases the rate of the transesterification reaction of the chosen oil into biodiesel as well as significantly reduces the amount of excess alcohol required for processing. It also increases the purity of the glycerin formed. This allows a change from the production from batch processing into continuous flow processing. Biodiesel is normally produced in batch reactors that use heat and mechanical mixing as its energy input.

Ultrasonic cavitation mixing achieves a better degree of mixing on a commercial scale. Ultrasonic mixing is an effective means to achieve better mixing levels in commercial processing. It provides the activation energy needed for the industrial transesterification process. Power ultrasonic reactors have been used to produce biodiesel through the methanolysis of soybean with sodium hydroxide as a catalyst. (Kumar and sharma, 2008).

When the reaction is carried out via ultrasonic wave, transesterification is efficiently activated, with short time of reaction. As the result, a drastic reduction in the quantity of by-product and a short separation time is obtained and at the same time can reduce the energy consumption. Biodiesel is primarily produced in the batch processes, in which a basic homogenous catalyst is introduced to catalyze the reaction. Ultrasound allows for the continuous processing. Besides reducing the reaction time, ultrasonication also reduces the separation time compared to the conventional agitation method.

When using the ultrasonication, the amount of excess alcohol required can be reduced. Most commonly, the sonication is performed at an elevated pressure (1 to 3 bar, gauge pressure) using a feed pump. Industrial biodiesel processing does not require much ultrasonic energy. In addition, ultrasonication is an effective means to increase the reaction speed and conversion rate in the commercial processing.

Figure 2.3 shows the typical result of the transesterification of rapeseed oil with potassium hydroxide studied by Carmen Stavarache. The blue line is the control sample, was exposed to intense mechanical mixing while the red line represent the sonicated sample with respect to the volume ratio, catalyst concentration and temperature. The horizontal axis shows the time after mixing or sonication, respectively. The vertical axis shows the volume of glycerin that settled at the bottom. This is the simple means of measuring the reaction speed. In this diagram, the sonicated sample (red line) reacts much faster than the control sample (blue line).

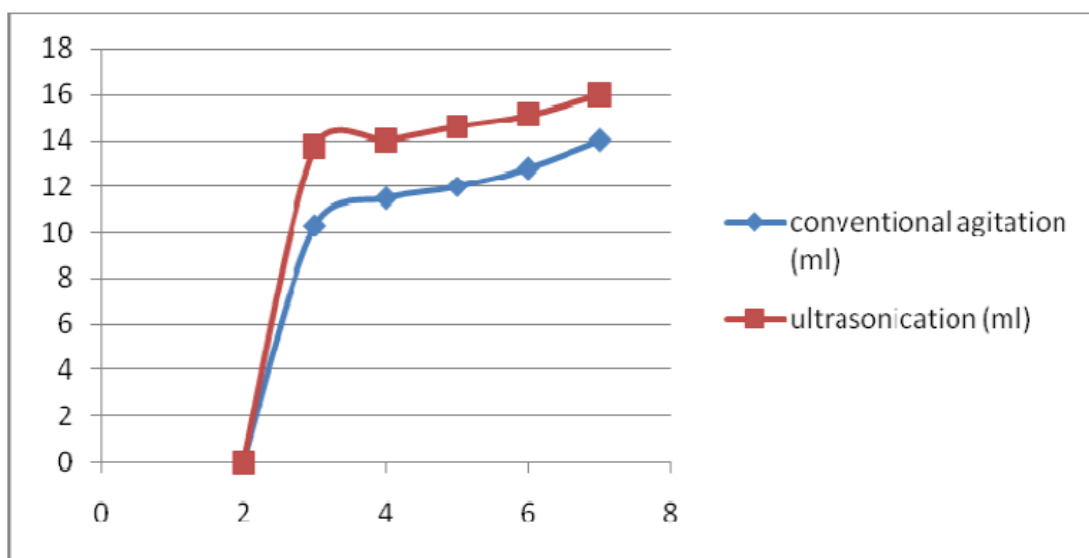


Figure 2.3: Result of rapeseed oil transesterification with potassium hydroxide using conventional agitation and ultrasonication

2.10 Ultrasound

Ultrasound is the process of propagation of the compression (rarefaction) waves with frequencies above the range of human hearing (above 15-16 KHz) (Shutilov,1998). Typical commercial ultrasonic instruments known as “probe system” have a piezoelectric transducer powered by a generator that couples energy into chemical reaction by means of horn or velocity transformer. The converter vibrates in a longitudinal direction and transmits this motion to the horn tip immersed in the solution, causes cavitation

Cavitation implies the opening of holes in liquids. Depending on the circumstances, this holes can be filled either by gases already dissolved in the liquid, in which case the phenomenon is sometimes called as gaseous cavitation or pseudocavitation, or, in the absence of such dissolved gases, by the vapor of the liquid itself (vapor cavitation or true cavitation). It is quite clear that the conditions for the appearance of these two kinds of cavitation can be quite different.

The applications of ultrasound in chemical processing enhance both the mass transfer and chemical reactions, this science called as sonochemistry. It offers the potential for shorter reaction cycles, cheaper reagent and less extreme physical conditions, leading to less expensive and perhaps chemical producing smaller plant. Existing literature on sonochemical reacting system is chemistry-intensive, and applications of this novel mean of reaction in remediation and pollution prevention seems almost unlimited. For example, environmental sonochemistry is a rapidly growing area that deals with the destruction of organic in aqueous solutions. However, some theoretical and engineering aspects are not yet fully understood (Adewuyi, 2001).

The cavitation phenomenon is also accompanied by the emission of visible radiation, which is given the name sonoluminescence. Some researchers take advantage of this phenomenon doing estimation of the bubbles collapse conditions from the intensity of the light emitted by the system, this area are being explored too.

Another important phenomenon called “acoustic streaming”, has been identified when ultrasound is applied to liquid systems. It consists mainly of a hydrodynamic vertical flow near the sound source and its intensity depends on the ability of the medium to absorb the acoustic energy (usually the energy absorbed by the medium generates an increase in temperature). This ability can be modified by the presence of the electrolysis salts. Other undesired effect of the sonochemical processes are erosion of emitter and reactor surface, creation of noise and acceleration of by-product formation (Loning et al, 2002). For the ultrasound agitations case , ultrasound application generate shockwaves when they collapse by implosion, forcing the oil and methanol to join.

2.11 Acid-Catalyzed Pre-Treatment

When jatropha curcas oil is used, an acid catalyzed is preferred, but it requires more excess methanol, high pressure and high cost stainless steel equipments. In addition, the yield of the product is low when the common sulfuric acid is used. Hence, a combine process with acid catalyzed pre-treatment is developed to synthesize biodiesel from jatropha oil. The first step would be the esterification of FFAs with methanol by acid catalyst which is acid sulfuric (Yong *et al*,2007). At the second step, sodium hydroxide is added to catalyze the transesterification reaction in which TG is reacted with methanol. Without waste water, reusing the catalyst and low cost of reaction tank, these to steps shows the potential application in fuel industry.